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Instability Monitoring and Fermi Level Pinning in Phosphate Buffer Saline/Self Assembled Monolayer/Si Electrode System

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ABSTRACT

This paper presents a study of the various methods for monitoring the long-term instabilities, i.e. flat band voltage shifts or capacitance variations, in electrolyte/self-assembled-monolayer/Si capacitor. Such instabilities affect the use of such devices as biosensors. The flat-band voltage shift is typically observed when the capacitor is dipped in biological solutions such as Phosphate Buffer Saline (PBS) solution or other common buffers, even before adding the biomolecules target. Capacitance drifts are observed over a time scale of a few hours at room temperature. It was found that the instability figures were depended on the measurement method.

A comparative study was conducted between common flat band voltage and capacitance monitoring methods. The flat band voltage was extracted by the Mott-Schottky plot or extracted from the measured Capacitance vs. Voltage (CV) curve using the calculated flat band capacitance. The capacitance at fixed bias was extracted using electrochemical impedance spectroscopy (EIS) by fitting the measurement to a model assuming a capacitor in series to resistor.

Impedance spectroscopy under very low current was found to yield the most stable results, while the other methods showed a significant drift. It was found that the flat band voltage instabilities were lower for a higher concentration solution. Moreover, the flat band values became almost constant at about ~0.5 V (with an error of about 20-30 mV) after 60 minutes of measurement. Those results indicate on the generation of electrically active fast state at the interface causing Fermi level pinning; this effect occurs during the capacitance voltage scan. Note that, this is the first case that Fermi level pinning behavior is observed in the context of biosensors, while the device is dipped in a biological solution. The Fermi pinning phenomenon of semiconductor in electrolyte has been observed also in the past in the context of semiconductor/redox electrolyte interfaces.

In summary, it is suggested that it is preferable to measure capacitance at fixed bias, and that the most stable operating point is at, or near, the point of zero current.

1. Introduction

Recently it was proposed to use functionalized Electrolyte/Insulator/Silicon field effect devices where the insulator includes or solely made of Self Assembled Monolayer (SAM) as biosensor for bio-recognition reactions (namely ESS biosensor) [1]. SAM is an essential layer for linking biological elements to the silicon surface. Specific bio-molecule detection is based on the interaction between the sensing molecules and the analyte (e.g. anti-body/anti-gen, DNA hybridization etc.). That interaction may lead to electrostatic coupling between the charge of the attached bio-molecules and the semiconductor. The effect can be due to net charge or dipole change in the electrolyte near the surface, very close to the solid in a distance comparable or smaller than the Debye length in the electrolyte.

Enhancement in sensitivity can be achieved using ESS biosensor. The double-layer capacitance at the interface SAM/electrolyte is smaller (3-4 $\mu F/cm^2$) in comparison with the capacitance at the SiO_2/electrolyte interface (10-20 $\mu F/cm^2$) [2,3], and the capacitance of the monolayer can varied up to several $\mu F/cm^2$ according to the length of the chain. Therefore, improvement in sensitivity by factor of 10-30 can be expected.

One of the main problems in applying such devices is that under some operating conditions they exhibit instability and insufficient

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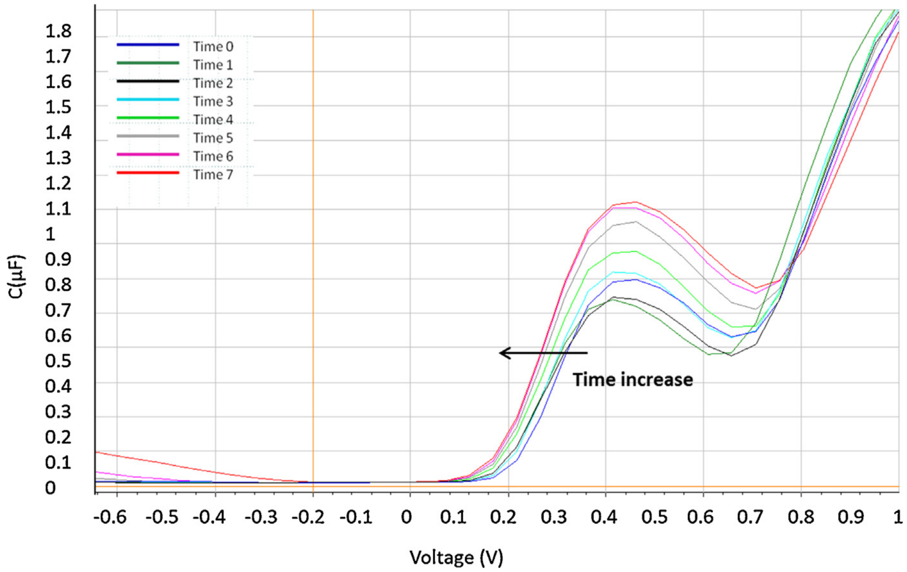

Fig. 1. C-V plots vs. time for an EIS device kept under open circuit potential in 0.1 M AF-PBS. The measurements were taken in 1-hour intervals over 7 hours at frequency of 1 kHz; the curve indicates lateral drift toward negative voltage.

reproducibility [4–11]. Such devices may also show poor yield and few critical failure modes that have not been fully understood. Therefore, it is critical to understand those behaviors before the addition of the biological target. In this work, we show that there are conditions and methods, where the devices are stable and can be used or characterized reproducibly.

Unchanged flat band voltage is one of the key requirements for the field effect device stability. There are few assumptions and physical models for that the flat band voltage variability, including, hydration of the SiO_2 that may affect on the flat band voltage of the EIS [12,13] and slow surface effects [14,15]; however, the most common postulate is that penetrations of ions to the SiO_2 layer are the main cause to the EIS instability [9,16,17]. In our previous work [18] we investigated the postulation that penetrations of alkali ions by diffusion to the thin underlying SiO_2 layer cause that instability. To prove this claim we performed Capacitance-Voltage (C-V) measurements in two buffers; the first one was the commonly used Phosphate Buffer Saline (PBS) while the other one was a novel buffer, Alkali Free PBS (AF-PBS). Next, the flat-band voltage drift with time was extracted (Fig. 1). The main conclusion was that the alkali ions in the buffer solution might affect the short-term stability, but not the long-term stability that is governed by another mechanism.

Following this conclusion, we expanded our investigation to reveal the source for the long-term instability. Our hypothesis was that the measurement method could affect the stability assessment of the device. Currently there is no consensus regarding the preferred method for electrolyte/insulator/semiconductor characterization or monitoring. C-V measurements provide a rapid, and rather accurate, evaluation of the flat-band shift; however, the applying voltage during the measurement affects the solid interface, for example by anodization or etching, introducing surface charge and surface states.

The alternative is using EIS measurements. In this case, the evaluation of the flat-band shift is not straightforward and we commonly follow the capacitance variations, which are function of the flat band voltage shifts. EIS analysis fits the data to an equivalent

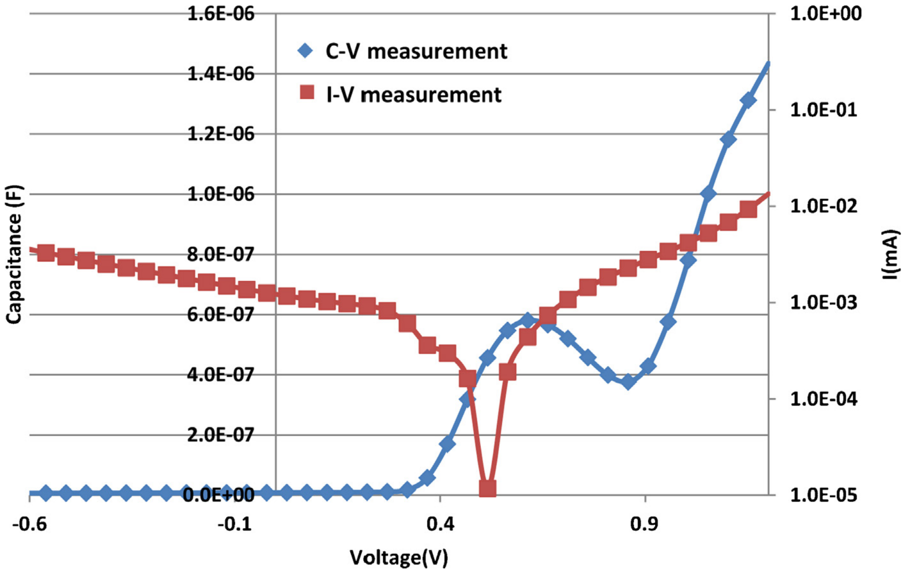

Fig. 2. C-V and I-V measurements performed at 1 kHz in 0.1M AF-PBS for the purpose of determining the measurement voltage for EIS.